First infrared high resolution analysis of the ν_5 band of phosgene $^{37}\text{Cl}_2\text{CO}$ J.-M. Flaud^a, F. Kwabia Tchana^a, A. Perrin^b, L. Manceron^{c,d}, M. Ndao^a^a Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA)/IPSL, UMR CNRS 7583, Universités Paris Est Créteil et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France^b Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539, Ecole Polytechnique, Université Paris Saclay, Palaiseau, France^c Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France^d MONARIS, CNRS UMR 8233, 4 Place Jussieu, F-75252 Paris Cedex, France

ARTICLE INFO

Article history:

Received 25 July 2017

Accepted 11 August 2017

Available online 15 August 2017

ABSTRACT

A Fourier transform spectrum of phosgene (Cl_2CO) has been recorded in the $11.8\ \mu\text{m}$ spectral region at low temperature and at a resolution of $0.00102\ \text{cm}^{-1}$ using a Bruker IFS125HR spectrometer coupled to synchrotron radiation leading to the observation of the ν_5 vibrational band of the isotopologue $^{37}\text{Cl}_2\text{CO}$. The corresponding upper state rovibrational levels were fit using a Watson-type Hamiltonian. In this way it was possible to reproduce the upper state rovibrational levels almost to within the experimental uncertainty i.e. $\sim 0.50 \times 10^{-3}\ \text{cm}^{-1}$. Very accurate rotational and centrifugal distortion constants were derived from the fit together with the following band center: $\nu_0(\nu_5, ^{37}\text{Cl}_2\text{CO}) = 848.970769\ (20)\ \text{cm}^{-1}$.

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1. Introduction

Phosgene, Cl_2CO , is an asymmetric top molecule and has been the topic of a number of microwave studies [1–5] in which the rotational ground state constants, as well as the first excited-state rotational constants of its various isotopic species were determined. In the infrared region, however, only a few studies have been performed. First the two bands, ν_1 and ν_5 of the most abundant isotopic species ($^{35}\text{Cl}_2\text{CO}$) were partly studied at high resolution using diode laser spectroscopy [5] and, then, were extensively analyzed using FTS spectra and synchrotron radiation from SOLEIL [6], where the corresponding bands of $^{35}\text{Cl}^{37}\text{ClCO}$ were also investigated.

This study led to an improved set of ground state rotational constants, as well as accurate constants of the upper states of these bands. Next, the corresponding line lists were used to retrieve phosgene profiles in the earth atmosphere from MIPAS spectra [7]. More recently the ν_3 and ν_6 bands were also analyzed at high resolution leading to accurate band centers and rotational constants for the corresponding upper vibrational states [8,9]. Finally a first detailed extensive analysis of the ν_2 and ν_4 bands of the two isotopologues $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$ was performed in the $580\ \text{cm}^{-1}$ region [10]. This paper presents the first detailed extensive analysis of the ν_5 band of $^{37}\text{Cl}_2\text{CO}$ in the $850\ \text{cm}^{-1}$ region for which the assignments have been extended to rather high quantum numbers despite the weakness of the band as compared to the ν_5 bands of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$ (Band intensity for $^{37}\text{Cl}_2\text{CO}$

about 10 times lower than the band intensity of the main isotopologue). The work was done using a high-resolution ($0.00102\ \text{cm}^{-1}$) Fourier transform spectrum recorded at a temperature of 169 K. The phosgene molecule $^{35}\text{Cl}_2\text{CO}$ has C_{2v} symmetry, and its structure as well as its symmetry properties and nuclear spin statistical weights are given in Ref. [6].

2. Experimental details

The high-resolution absorption spectrum of phosgene was recorded on the AILES Beamline at Synchrotron SOLEIL using the Synchrotron light source, coupled to the Bruker IFS125HR Fourier transform spectrometer [11,12] and a newly developed cryogenic multipass cell [13]. This spectrum was first recorded to analyse the ν_5 bands of the two main isotopologues [6] and the reader will find all the experimental details in this last reference. Fig. 1 gives an overview of the phosgene spectrum around $11.8\ \mu\text{m}$ showing the high signal-to-noise ratio which was obtained. At $11.75\ \mu\text{m}$ the distinctive shapes of the A-type ν_5 bands with their narrow Q-branches are clearly visible.

3. Assignments and results

The line assignment process proved to be difficult both because of the density of lines in the spectrum and because of the weakness of the ν_5 band of $^{37}\text{Cl}_2\text{CO}$ which is about 10 times weaker than the ν_5 band of the main isotopologue $^{35}\text{Cl}_2\text{CO}$. To start the assignment,

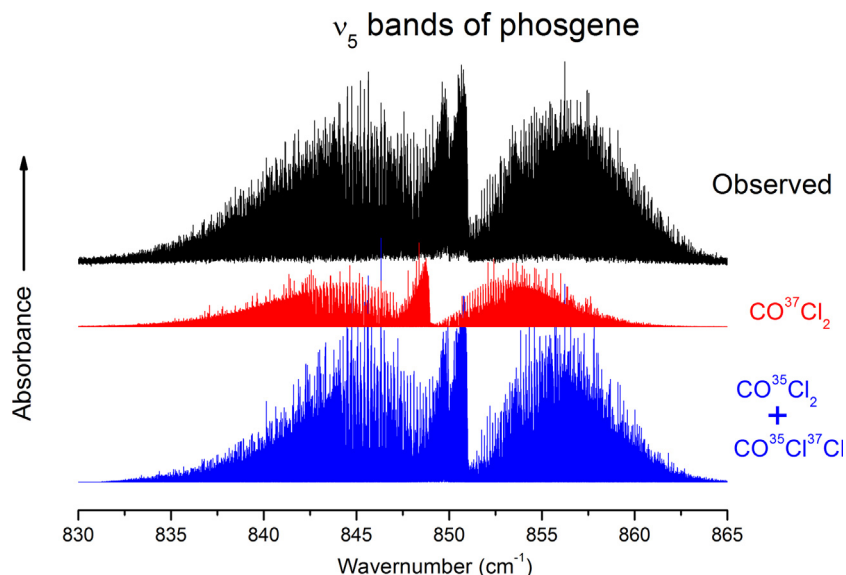


Fig. 1. Overview of the phosgene spectrum in the 11.8 μm spectral region. The distinctive shape of the A-type bands ν_5 of the three phosgene isotopologues with their narrow Q-branches clearly recognizable. Upper trace: observed spectrum recorded with a resolution of 0.00102 cm^{-1} , an optical path length of 3.14 m, a phosgene pressure of 2.5 (0.2) Pa and a stabilized temperature of 169 K. Lower traces: synthetic spectra, calculated at the same experimental conditions using the line lists generated in this work or in Ref. [6]. The observed and synthetic spectra are in absorbance ($-\ln(I/I_0)$) and shifted vertically for clarity.

Table 1

Watson's Hamiltonian used to calculate the 5^1 rovibrational levels of phosgene $^{37}\text{Cl}_2\text{CO}$.

Watson-type Hamiltonian:	
$H_W = E_v + [A^v - 1/2(B^v + C^v)]J_z^2 + 1/2(B^v + C^v)J^2 + 1/2(B^v - C^v)J_{xy}^2 - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v (J^2)^2 - \delta_K^v \{J_z^2, J_{xy}^2\} - 2\delta_J^v J_{xy}^2 J^2 + H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 + H_{JKJ}^v J_z^2 (J^2)^2 + H_J^v (J^2)^3 + h_K^v \{J_z^4, J_{xy}^2\} + h_{KJ}^v \{J_z^2, J_{xy}^2\} J^2 + 2h_J^v J_{xy}^2 (J^2)^2 + \dots$	
with $\{A, B\} = AB + BA$ and $J_{xy}^2 = J_x^2 - J_y^2$.	

we used for the Hamiltonian upper state constants values derived from the upper state constants of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$ [6]. As far as the band center is concerned its value was refined looking carefully at the Q branch in the experimental spectrum. The first assignments were performed for P and R lines with low K_a values. Then, as soon as a few lines were assigned, the corresponding upper state energy levels were fitted using a Watson-type Hamiltonian (Table 1) [14] and the refined upper state Hamiltonian

Table 2

Vibrational band center, rotational and centrifugal distortion constants (in cm^{-1}) for the 5^1 vibrational state of phosgene $^{37}\text{Cl}_2\text{CO}$.

	$^{37}\text{Cl}_2\text{CO}$	
	0^0	5^1
E_v/hc		848.970769(20) ^a
$A \times 10^1$	2.60664995(120)	2.59448852(410)
$B \times 10^1$	1.09654444(420)	1.09377506(160)
$C \times 10^1$	0.770940179(440)	0.766981671(690)
$\Delta_K \times 10^6$	0.339669648(2700)	0.3844256(7200)
$\Delta_{JK} \times 10^7$	−0.47510876(4900)	−0.894705(4900)
$\Delta_J \times 10^7$	0.294336592(6600)	0.2926131(8700)
$\delta_K \times 10^7$	0.59132664(4500)	0.538022(7600)
$\delta_J \times 10^7$	0.101790358(1600)	0.101037(4800)
$H_{KJ} \times 10^{11}$	0.1506305(5800)	^b
$H_{JK} \times 10^{11}$	0.0581747(4100)	^b
$H_J \times 10^{13}$	0.8556 ^c	^b
$h_K \times 10^{11}$	−0.229577(1700)	^b
$h_{KJ} \times 10^{12}$	0.8414 ^c	^b

^a Uncertainties are given in parentheses in units of the last significant digits as stated, in terms of one standard deviation σ in the least squares adjustment.

^b Fixed at ground state values.

^c Fixed at ground state values of $^{35}\text{Cl}_2\text{CO}$ [6].

Table 3

Range of quantum numbers observed for experimental energy levels of the vibrational state 5^1 of $^{37}\text{Cl}_2\text{CO}$.

	$^{37}\text{Cl}_2\text{CO}$
Vibrational state	5^1
Number of energy levels	289
J_{max}	51
K_{max}	37
Std. deviation (10^{-3} cm^{-1})	0.50

constants were used to perform more reliable predictions, allowing one to assign new lines. The assignment process was iterated until no new assignment could be done. The band center, rotational and centrifugal constants for the 5^1 vibrational state of $^{37}\text{Cl}_2\text{CO}$ are given in Table 2. The fit is rather satisfactory since, due to the weakness of the band, the standard deviation is only about twice the experimental uncertainty (Table 3). Figs. 2 and 3 show comparisons of the observed and calculated spectra. The good agreement between observation and simulation demonstrates the quality of the analysis and the fitting.

4. Summary

Using a high-resolution Fourier transform spectrum an extensive analysis of the ν_5 band of phosgene $^{37}\text{Cl}_2\text{CO}$ has been performed. The upper state rovibrational energy levels of the 5^1 upper vibrational state of this isotopologue have been fitted almost to within the experimental accuracy using a Watson-type

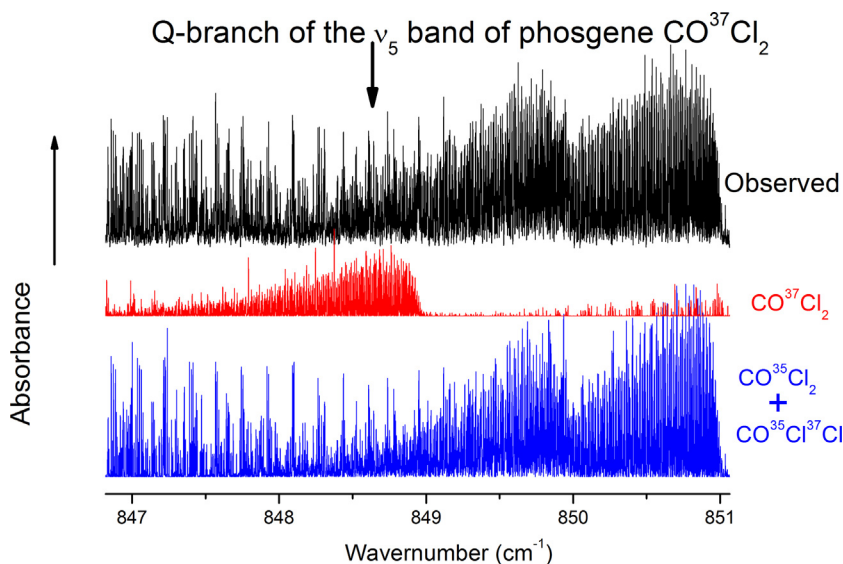


Fig. 2. The Q-branch of the ν_5 bands of $^{35}\text{Cl}_2\text{CO}$, $^{35}\text{Cl}^{37}\text{ClCO}$ and $^{37}\text{Cl}_2\text{CO}$. Upper trace: observed spectrum with the same experimental conditions as in Fig. 1. Lower traces: synthetic spectra calculated as in Fig. 1.

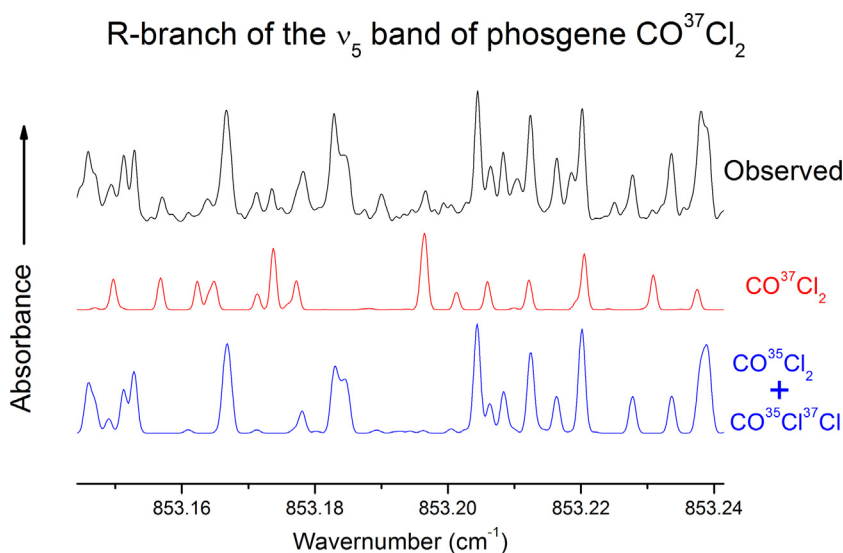


Fig. 3. Portion of the R-branches of the ν_5 bands of $^{35}\text{Cl}_2\text{CO}$, $^{35}\text{Cl}^{37}\text{ClCO}$ and $^{37}\text{Cl}_2\text{CO}$. Upper trace: observed spectrum with the same experimental conditions as in Fig. 1. Lower trace: synthetic spectra calculated as in Fig. 1.

Hamiltonian. In this way, accurate band center, rotational and centrifugal distortion constants have been determined.

Acknowledgements

Part of this work was supported by the European Space Agency through contract N° 21719/08/I-OL, “Support to MIPAS Level 2 Product Validation”. One of authors (JMF) thanks the Sensor Science Division for support during a stay at NIST.

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